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On the correlation of the abundances of HNCO and NH_2CHO: Advantages of solid *para*-H_2 to study astrochemical H-atom addition and abstraction reactions

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Abstract. In dense interstellar clouds that are shielded from high-energy radiation (e.g., UV photons or cosmic rays), H-atom addition and abstraction reactions that take place on grain surfaces play principal roles in the synthesis or decomposition of complex organic molecules (COMs). These reactions are extensively investigated with laboratory experiments by bombarding astrophysical analogue ices with a beam of low-temperature H atoms. Here we demonstrate that, although 2-4 K solid *para*-H_2 does not represent a typical environment of the surface of interstellar grains, *para*-H_2 matrix isolation combined with IR spectroscopy is a complementary tool to sensitively detect astrochemical hydrogenation and dehydrogenation processes.

Keywords. astrochemistry, molecular processes, ISM: clouds

H atoms can be conveniently generated in solid *para*-H_2 by simple photolytic methods (Raston & Anderson (2006); Bahou *et al.* (2014)), e.g., by UV photolysis of Cl_2, premixed with *para*-H_2 before deposition, followed by IR irradiation. Since the solid *para*-H_2 is a soft quantum matrix, due to the excess energy of the photons, the two Cl atoms can be separated and occupy two separate sites. Therefore, unlike in other matrix hosts, the two fragments might be isolated in *para*-H_2. This is the so-called diminished cage effect. Since the $H_2 + Cl \rightarrow HCl + H$ reaction has a substantial barrier, it does not take place spontaneously in solid *para*-H_2. However, it can be initiated by IR irradiation that leads to vibrationally excited *para*-H_2 molecules.

After production, H atoms can move in solid *para*-H_2 by a quantum diffusion mechanism. Briefly, the H atom can react with a neighboring *para*-H_2 molecule, which results in the formation of H_2 and an H atom. The product H atom is therefore formed in the site next to the one occupied by the reactant H atom. This mechanism resembles the Grotthuss mechanism (de Grotthuss (1806)), i.e., the diffusion of protons in water. Although the $H + H_2 \rightarrow H_2 + H$ reaction has an activation barrier 40 kJ mol^{-1}, the reaction, and therefore the diffusion of H atoms is feasible even near 0 K due to quantum tunneling (Fushitani & Momose (2003)). Finally, the diffusing H atoms can come into contact with other dopants and react.

The method is complementary to the typical astrophysical experiments of ice analogues with some advantages. With the above production method, H atoms can be produced in solid *para*-H_2 in a relatively high mixing ratio. Since *para*-H_2 interacts with dopants via only extremely weak intermolecular forces, the species isolated in a *para*-H_2 matrix are nearly unperturbed, so that their spectral features in the IR region are very sharp. These advantages together with the efficient diffusion of H atoms make it possible to follow the H-addition and abstraction reactions very sensitively on the laboratory time scale, and make the IR spectroscopic identification of the reaction products unambiguous.

The two main limitations of this method for investigation of astrochemical processes are the apolar medium and a temperature lower than the typical temperature of grain surfaces. In a more polar environment of astrophysical ices, the H atoms of a molecule might be blocked by intermolecular interactions, hence decreasing its reactivity. The higher temperature of ice might make feasible reaction channels that are inaccessible at 2-4 K in solid *para*-H_2. Therefore, the experiments in *para*-H_2 can elegantly prove if a reaction can take place at a low temperature limit, but the observed reaction rates are likely not the same as in astrophysical conditions.

In order to demonstrate the applicability of this method, we briefly discuss the H abstraction and addition reactions of formamide (H_2NCHO) and isocyanic acid (HNCO) in solid *para*-H_2. (See details of this investigation in Haupa *et al.* (2019)). H_2NCHO, the smallest molecule possessing an amide group, was first detected toward Sagittarius B2 almost 50 years ago (Rubin *et al.* (1971)). It was found later in various pro- and pre-stellar objects (Bianchi *et al.* (2018)) and comets (Biver *et al.* (2014)). A number of studies have focused on its formation mechanism. Laboratory experiments demonstrated that it can be formed on the grain surfaces e.g., from ammonia and carbon monoxide upon electron impact (Jones *et al.* (2011)). Recent astronomical observations found nearly linear correlation between the abundance of H_2NCHO and HNCO over six orders of magnitude in luminosity (Bisschop *et al.* 2007; López-Sepulcre *et al.* (2015)). This correlation has been confirmed with analysis of D/H isotopic ratios of both species obtained from ALMA observations (Coutens *et al.* (2016)). This tight correlation likely reveals that HNCO and H_2NCHO are linked by chemical reactions in the interstellar medium (ISM). López-Sepulcre and coworkers (2015) proposed that consecutive hydrogenation of HNCO is likely to form H_2NCHO. However, Noble and coworkers (2015) bombarded H atoms onto pure HNCO ice, but observed neither H_2NCO nor H_2NCHO.

We have investigated the reaction of H_2NCHO and H atoms in solid *para*-H_2. Among the reaction products, aminocarbonyl radical (H_2NCO) and HNCO could be clearly identified. A number of experiments with different H atom/H_2NCHO ratios were performed. In the case of high H-atom mixing ratios, the [HNCO]/[H_2NCHO] ratio increased over unity, and after reaching a maximum, a decrease in the mixing ratio of HNCO and H_2NCO and the reproduction of H_2NCHO were observed. The experiment was repeated by using D_2NCHO. In this case, HNCO, DNCO, D_2NCO, (*E*) and (*Z*)-HDNCO, and *cis* and *trans*-HDNCHO were identified among the reaction products. The observed isotopologues support a dual-cycle H-addition/abstraction mechanism that is depicted for a generalized case in Fig. 1.

In the case of X=HNCO and XH_2=H_2NCHO, the above dual-cycle mechanism satisfactorily links chemically the interstellar HNCO and H_2NCHO. The observations also show that the quasi-equilibrium is shifted towards HNCO because of a small barrier for the reaction H + HNCO → H_2NCO. Similar dual-cycle mechanism might link also other unsaturated/saturated pairs of interstellar molecules; e.g., recent studies indicated the existence of similar cycles among CO, H_2CO and CH_3OH (Chuang *et al.* (2016)), as well

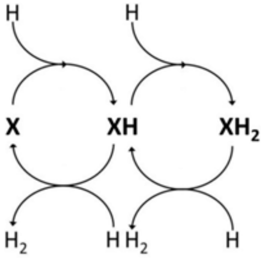

Figure 1. Generalized dual-cycle mechanism of H-atom addition and abstraction of unsaturated/saturated pairs of molecules.

as between polyaromatic hydrocarbons (PAHs) and their partially hydrogenated forms (Raus & Hornekær (2008); Menella *et al.* (2012); Cazaux *et al.* (2019)). Therefore, this mechanism can contribute to the formation of H_2 molecules on the surface of interstellar grains.

We propose that potential astrochemically relevant H-atom addition and abstraction reactions may be investigated by this method. Reactions that were reported to take place in one direction (typically addition) might also take place in the "reverse" (abstraction) direction, which might have been overlooked previously.

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